

Response of Bi-disperse Polyelectrolyte Brushes to External Electric Fields — A Numerical Self-consistent Field Theory Study*

Cong Kang^a, Shuang-liang Zhao^b and Chao-hui Tong^{a**}

^a Department of Physics, Ningbo University, Ningbo 315211, China

^b College of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

Abstract The self-consistent field theory has been employed to numerically study the response of bi-disperse flexible polyelectrolyte (PE) brushes grafted on an electrode to electric fields generated by opposite surface charges on the PE-grafted electrode and a second parallel electrode. The numerical study reveals that, under a positive external electric field, the shorter and negatively charged PE chains are more responsive than the longer PE chains in terms of the relative changes in their respective brush heights. Whereas under a negative external electric field, the opposite was observed. The total electric force on the grafted PE chains was calculated and it was found that, under a positive external electric field, the magnitude of the total electric force acting on one shorter PE chain is larger than that on one longer PE chain, or vice versa. The underlying mechanism was unraveled through analyzing the total electric field across the two oppositely charged electrodes.

Keywords Polyelectrolyte brushes; Self-consistent field theory; Electrical stimulus; Polydispersity

INTRODUCTION

Polyelectrolyte (PE) brushes, charged polymer chains densely anchored on solid substrate through chemical bond, have emerged as a class of promising smart materials. PE brushes can be used to modify and regulate the material surface properties, and have found many technological applications^[1–15]. One important application of PE brushes is in sensing and actuation because the grafted polymer chain conformations can be adjusted and tuned by external stimuli. In particular, the response of PE brushes to electrical stimulus, *i.e.*, an electric field applied normal to the grafting substrate, provides an advantageous and convenient way to regulate the polymer chain conformations. Experimental demonstration of the response of PE brushes to external electrical stimulus has been presented in the literatures^[16–18].

Due to their technological importance, the response of PE brushes to an externally applied electric field has been intensely studied by theories, numerical calculations and computer simulations^[19–27]. Among these studies, self-consistent field theory (SCFT) and molecular dynamics simulation are the two most frequently employed methods^[21–27]. Nevertheless, in all of the theoretical and computational studies of the response of PE brushes to external electric fields, the charged polymer chains were assumed to be monodisperse, that is, all of the grafted polymer chains are of equal chain length. In reality, however, polydispersity is a rule rather than the exception for all of the synthetic polymers, despite the great progress being made in synthesizing polymers with polydispersity index approaching unity. Therefore, it is imperative to investigate the effect of polydispersity on

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** Corresponding author: Chao-hui Tong (童朝晖), E-mail: tongchaoahui@nbu.edu.cn

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the response of PE brushes to external electric fields.

Another motivation of this study is due to an interesting experiment in which single-stranded DNA (ssDNA) of different lengths tethered to an Au electrode can be separated by applying an external electric field^[16–18]. The external electric field was manipulated by gradually diluting the buffer solution with which the Au electrode was in contact, thus generating a strong yet evolving non-uniform electric field near the Au electrode. By gradually decreasing the ion concentration, thus increasing the strength of the electric field, longer ssDNA strands were detached first and then followed by shorter ones. A numerical analysis based on a simple electric double layer model was performed, which provided a semi-quantitative explanation of the experimental results.

In this paper, we present a numerical SCFT study of the response of bi-disperse PE brushes grafted on an electrode to external electric fields. The external electric field is generated by the opposite surface charges on the grafting electrode and a second parallel electrode. In the brush system sandwiched between the two electrodes, no salt ions were added. Particular attention was paid to the total electric force acting on both the shorter and longer PE chains, thus making direct contact with the experiment sorting ssDNA based on length using electric fields.

THEORY, MODEL EQUATIONS AND NUMERICAL METHODS

In this paper, we consider a system of strong (completely ionized) PE brushes sandwiched between two parallel planar electrodes with a separation D . A Cartesian coordinate system was constructed such that the x axis is normal to the electrodes. The two electrodes were assumed to be connected to an external electric circuit driven by an electric power source, resulting in a surface charge density of σ_e (in units of number of elementary charges per unit area) and $-\sigma_e$ on the electrodes at $x = 0$, $x = D$, respectively. Two kinds of chemically identical homopolymer chains A, B with chain lengths of N_A , N_B , were uniformly grafted onto the electrode at $x = 0$. Let's denote $\alpha = N_B/N_A$ and write $N_A = N$. The grafting densities of chain types A, B are denoted as σ_{gA} , σ_{gB} , respectively (in units of number of chains per unit area). The average degrees of ionization of PE chains of both types with the smeared charge distribution were assumed to be the same and are denoted as α_p . The monomers carry negative charges and release positive monovalent counterions into the aqueous solution. In this study, no salt ions were introduced to the aqueous solution sandwiched between the two electrodes. Ignoring the edge effect of the electrodes, the problem can be reduced from three-(3D) to one-dimensional (1D), and each 3D physical quantity can be viewed as a 1D property on a per unit area in the x direction basis.

The self-consistent field theory is a well-established mean-field theory very suitable for the study of phase behaviors and equilibrium thermodynamics of multi-component neutral/charged polymeric systems^[28, 29]. Within SCFT, the SCF equations are summarized as follows:

$$\phi_A(\vec{r}) + \phi_B(\vec{r}) + \phi_S(\vec{r}) - 1 = 0 \quad (1)$$

$$\omega_A(\vec{r}) = \chi_{ps} N \phi_S(\vec{r}) + \eta(\vec{r}) \quad (2)$$

$$\omega_B(\vec{r}) = \chi_{ps} N \phi_S(\vec{r}) + \eta(\vec{r}) \quad (3)$$

$$\omega_S(\vec{r}) = \chi_{ps} N \phi_A(\vec{r}) + \chi_{ps} N \phi_B(\vec{r}) + \eta(\vec{r}) \quad (4)$$

$$\omega_{\pm}(\vec{r}) = N v_{\pm} \psi(\vec{r}) \quad (5)$$

$$\phi_A(\vec{r}) = \frac{\bar{\phi}_A}{Q_A} \int_0^1 ds_A q_A^g(\vec{r}, s_A) q_A^f(\vec{r}, 1 - s_A) \quad (6)$$

$$\phi_B(\vec{r}) = \frac{\bar{\phi}_B}{\alpha Q_B} \int_0^{\alpha} ds_B q_B^g(\vec{r}, s_B) q_B^f(\vec{r}, \alpha - s_B) \quad (7)$$

$$\phi_M(\vec{r}) = \frac{\bar{\phi}_M}{Q_M} \exp[-\omega_M(\vec{r})/N] \quad (8)$$

$$\vec{\nabla} \cdot [\varepsilon(\vec{r}) \vec{\nabla} \psi(\vec{r})] = -N [\alpha_p v_A \phi_A(\vec{r}) + \alpha_p v_B \phi_B(\vec{r}) + v_+ \phi_+(\vec{r}) + v_- \phi_-(\vec{r})] \quad (9)$$

where $\phi_j(\vec{r})$ with $j = A, B, S$ and $\pm$ are the dimensionless volume fractions of PE chains, solvent molecules and mobile ions, $\eta(\vec{r})$ is the Lagrange multiplier to enforce the incompressible condition, χ_{PS} notes the Flory-Huggins interaction parameter between monomers and solvent molecules. A, B polymer chains have the same Kuhn length (monomer size) a , and the solvent molecules were assumed to have the same size as monomers. The mobile ions are point-like particles. In the above equations, the volume-averaged densities $\bar{\phi}_A \equiv n_A N / (\rho_0 V)$, $\bar{\phi}_B \equiv n_B N / (\rho_0 V)$, and $\bar{\phi}_M \equiv n_M / (\rho_0 V)$, where n_A , n_B and n_M are the total numbers of grafted PE chains (types A, B) and species M ($M = S, +$ and $-$), and V denotes the total volume of the system. $\varepsilon(\vec{r})$ is the dielectric permittivity. $Q_A = \int d\vec{r} q_A^g(\vec{r}, 1) / V$, $Q_B = \int d\vec{r} q_B^g(\vec{r}, \alpha) / V$, $Q_M = \int d\vec{r} \exp[-\omega_M/N] / V$. ρ_0 denotes the same density of PE segments and the solvent molecules. Note that $\rho_0 = a^{-3}$. In Eq. (9) $v_A \equiv v_B \equiv v_p = -1$, $v_{\pm} = \pm 1$ are for the charge valences of PE chains and the mobile ions, respectively. For the present study, the only mobile ions are positively charged monovalent counterions.

The propagators $q_A(\vec{r}, s_A)$, and $q_B(\vec{r}, s_B)$ represent the probability of finding the segment $s_{A(B)}$ at the position $\vec{r}$, which respectively satisfy the following modified diffusion equations:

$$\frac{\partial q_A(\vec{r}, s_A)}{\partial s} = \nabla^2 q_A(\vec{r}, s_A) - [\omega_A(\vec{r}) + N \alpha_p v_A \psi(\vec{r})] q_A(\vec{r}, s_A) \quad (10)$$

$$\frac{\partial q_B(\vec{r}, s_B)}{\partial s} = \nabla^2 q_B(\vec{r}, s_B) - [\omega_B(\vec{r}) + N \alpha_p v_B \psi(\vec{r})] q_B(\vec{r}, s_B) \quad (11)$$

with the initial condition $q_{A(B)}^g(x = \Delta x, s = 0) = 1$ and $q_{A(B)}^f(x, s = 0) = 1$, and the boundary condition $q_{A(B)}^f(x = 0, s) = 0$, $q_{A(B)}^f(x = D, s) = 0$, $q_{A(B)}^g(x = 0, s) = 0$, $q_{A(B)}^g(x = D, s) = 0$ on the surfaces of the two electrodes.

In the present study, the chain lengths of bi-disperse flexible brushes are in the range of 20 to 150 with a fixed monomer size of $a = 0.7$ nm. The chain length of type A was fixed as $N_A \equiv N = 50$ throughout this study. We scale all lengths in the system by the radius of gyration of a neutral Gaussian chain of chain length of N ($R_g^0 \equiv a\sqrt{N/6}$) except for the surface charge and grafting densities. The product of the surface charge density σ_e of the grafting electrode and a^2 , which is defined as the dimensionless surface charge density, was varied from -4.76×10^{-2} to $+1.90 \times 10^{-1}$, which corresponds to a charge density of $-9.72 \times 10^{-2} \text{ nm}^{-2}$ to $+3.89 \times 10^{-1} \text{ nm}^{-2}$ or $-1.55 \times 10^{-2} \text{ C/m}^2$ to $+6.22 \times 10^{-2} \text{ C/m}^2$. The dimensionless grafting density $\sigma_{gA(B)} a^2$ was varied from 0.05 to 0.1 (or from 1.02×10^{17} grafted chains/m² to 2.04×10^{17} grafted chains/m²). The average degree of ionization was fixed as $\sigma_p = 0.1$. Because the electrostatic interactions in the system under external electric fields are the main focus of this study, for simplicity, all of the Flory-Huggins parameters were set to zero. Moreover, the dielectric property of the brush system was assumed to be homogeneous and the dielectric permittivity of the system was set to be the same as that of pure water at room temperature. In Eq. (9) which is in a dimensionless form, the dimensionless dielectric permittivity is $\varepsilon = 6\varepsilon_0 \varepsilon_s k_B T a / e^2$ where ε_0 , ε_s , k_B , T and e are respectively the vacuum permittivity, the dielectric constant of water, Boltzmann constant, the absolute temperature and the elementary charge. In the numerical calculations, ε was set to 0.476 which corresponds to $\varepsilon_s = 78$ and $T = 293$ K (K refers to Kelvin). The dimensionless electric potential ψ (referred to as $\psi_{\text{dimensionless}}$) in Eq. (9) is related to electric potential ψ in units of volts as $\psi_{\text{dimensionless}} = e\psi/k_B T$. After obtaining the electric potential profile from numerically solving Eq. (9), the dimensionless electric field E was then calculated by $E = -d\psi/dx$ (ψ and x are dimensionless). In presenting numerical results regarding electric field in the subsequent section, the dimensional

electric field in units of V/m was used and it was obtained from the dimensionless electric field through $E = k_B T E_{\text{dimensionless}} / (e R_g^0)$. A dimensionless electric field strength of 1 corresponds to an electric field strength of about 1.25×10^7 V/m. Also in presenting results in Figs. 5–8 in the subsequent section, the length scale has been transformed from R_g^0 to monomer size a . It should be pointed out that, it is a common practice to use the radius of gyration of a neutral Gaussian chain rather than the monomer size to scale all lengths in numerically solving SCF equations^[28, 29]. Unless otherwise stated, the separation between the two oppositely charged electrodes D was fixed at $32R_g^0$ at $N = 50$.

The brush height $H_{A(B)}$ is calculated from the following expression:

$$H_{A(B)} = 2 \sqrt{\frac{\int_0^D x^2 \phi_{A(B)}(x) dx}{\int_0^D \phi_{A(B)}(x) dx}} \quad (12)$$

To compare the responses of the two types of grafted PE chains to external electric fields, the relative change in the brush height denoted by $\Delta H/H_{A(B)}^0$ is invoked, in which $H_{A(B)}^0$ refers to the brush height in the absence of external electric fields.

The total electric force acting on the grafted PE chains is obtained as follows:

$$F_{A(B)} = \int_0^D \phi_{A(B)}(x) \alpha_p E(x) dx \quad (13)$$

Note that the electric field in the above equation is computed from $E(x) = -d\psi(x)/dx$. A dimensionless total electric force of 1 corresponds to 1.2×10^7 N/m².

The SCF equations were numerically solved by the standard numerical techniques^[27]. The grid size of the computational domain is $\Delta x = R_g^0/16$ and the pseudo-time step size is $\Delta s = 1/800$. Note that the grafting point is shifted from the grafting substrate by one lattice space Δx .

RESULTS AND DISCUSSION

Effect of External Electric Fields on the Brush Height

Because the monomers are negatively charged, the grafted PE chains will be stretched under a negative external electric field corresponding to a negatively charged grafting electrode, leading to an increase in the brush height, or vice versa. It can be clearly seen from Figs. 1 and 2 that, under a positive external electric field, the brush height decreases with increasing strength of the electric field. Taking the brush height in the absence of external electric fields as a reference, the relative change in the brush height is more significant for PE chains with shorter chain length in the bi-disperse polyelectrolyte brush system under a positive external electric field as revealed from Figs. 1 and 2. Moreover, it can be seen by comparing Fig. 1 with Fig. 2 that, for the collapse of the bi-disperse PE brushes system under a positive external electric field, the response of PE chains with longer chain length in terms of the relative change in the brush height will become weaker as its chain length gets longer. It was found that the brush heights of both the shorter and longer chains decrease with increasing grafting density but the trends shown in Figs. 1 and 2 are not altered by changing the grafting density of either or both types of chains.

On the contrary, for the stretching of grafted PE chains under a negative external electric field, the relative change in the brush height is more significant for PE chains with longer chain length. Furthermore, Figs. 1 and 2 clearly show that, in terms of the magnitude of the gradient of the plot of relative change in the brush height against the external electric field, the degree of extension of the longer PE chains under a negative external electric field is higher than that of the collapse under a positive external electric field. Due to the numerical stability, the negative external electric field was only explored up to -2.2×10^7 V/m for the system of parameters in Fig. 2. With increasing chain length of the longer PE chains in the bi-disperse brushes system, the issue of numerical stability exacerbates (comparing the left ends of the x axis of Figs. 1 and 2). Our algorithm converged

very nicely in the whole range of positive surface charge densities (or up to 9.0×10^7 V/m). The rather poor convergence in the case of bi-dispersed PE brushes system under a negative external electric field can be attributed to the fact that the negatively charged PE chains are grafted onto negatively charged electrode and the grafting point is only one lattice spacing Δx from the grafting electrode in the algorithm. Grafting negatively charged PE chains onto negatively charged electrode is very energetically unfavorable compared with the case of grafting negatively charged PE chains onto positively charged electrode.

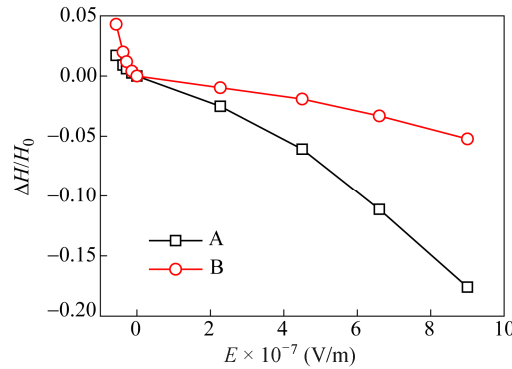


Fig. 1 Relative change in the brush height plotted against the strength of the external electric field

The system parameters are $\alpha_p = 0.1$, $\sigma_{gA} = 0.05$, $\sigma_{gB} = 0.05$, $N_A = 50$ and $N_B = 100$. In the figure, the curve with square symbols corresponds to PE chains of type A and the curve with circle symbols represents PE chains of type B. The brush heights in the absence of external electric fields of type A and B are $H_A^0 = 14.36a$ and $H_B^0 = 42.54a$, respectively.

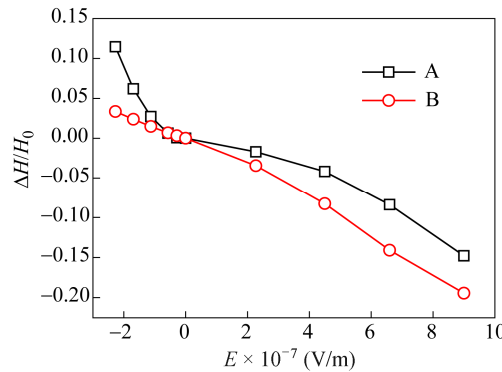


Fig. 2 Relative change in the brush height plotted against the strength of the external electric field

The system parameters are $N_A = 50$, $N_B = 20$, $\alpha_p = 0.1$, $\sigma_{gA} = 0.05$ and $\sigma_{gB} = 0.05$. The brush heights in the absence of external electric fields of type A and B are $H_A^0 = 20.92a$ and $H_B^0 = 6.85a$, respectively.

Effect of External Electric Fields on the Total Electric Force Acting on Grafted PE Chains

It can be clearly seen from Figs. 3 and 4 that the plot of the total electric force acting on grafted longer PE chains is on top of that of grafted shorter PE chains. In the absence of external electric field, the total electric force acting on the grafted shorter PE chains is about zero, whereas the total electric force on grafted longer PE chains is positive, which means that the total electric force acting on grafted longer PE chains points in the chain stretching direction. Under a positive external electric field, the sign of the total electric force on grafted shorter chains is negative, thus the electric force tends to attract the grafted shorter chains towards the positively charged grafted electrode, leading to a decrease in the brush height. Moreover, the magnitude of the electric force increases with increasing strength of the external electric field. On the other hand, for the grafted longer PE chains, the sign of the total electric force becomes negative only when the positive external electric field exceeds a certain threshold. Evidently, in a strong positive external electric field, the strength of the total electric force acting on the grafted shorter PE chains is larger than that on the grafted longer PE chains, meaning that the

grafted shorter PE chains are more strongly attracted towards the grafting electrode than the longer PE chains. This finding is consistent with the result that, under a positive external electric field, shorter PE chains are more responsive than longer chains in terms of the relative change in the brush height.

Under a negative external electric field, the sign of the total electric force for either type of the grafted PE chains is positive. Thus, the electric force tends to stretch the grafted PE chains. Obviously, under a negative external electric field, the strength of the total electric force acting on grafted longer PE chains is larger than that on grafted shorter PE chains, meaning that the grafted longer PE chains are more strongly stretched than the shorter PE chains, which is in line with the results shown in Figs. 1 and 2.

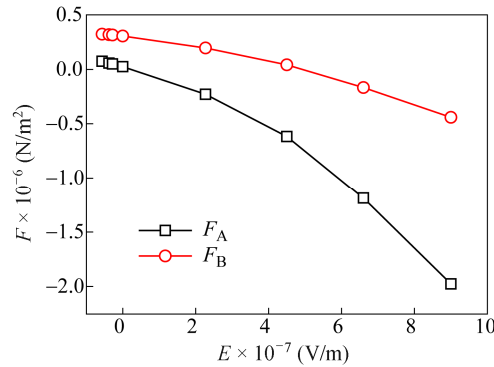


Fig. 3 Plots of the total electric force acting on grafted PE chains against the strength of the external electric field for the two types of grafted PE chains with different chain lengths
The system parameters are $N_A = 50$, $N_B = 100$, $\alpha_P = 0.1$, $\sigma_{gA} = 0.05$ and $\sigma_{gB} = 0.05$.

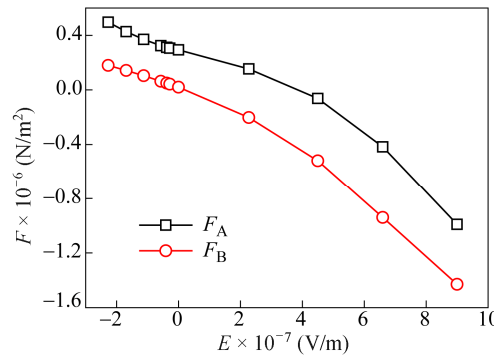


Fig. 4 Plots of the total electric force acting on grafted PE chains against the external electric field for the two types of grafted PE chains with different chain lengths
The system parameters are $N_A = 50$, $N_B = 20$, $\alpha_P = 0.1$, $\sigma_{gA} = 0.05$ and $\sigma_{gB} = 0.05$.

Distribution of Monomers, Counterions and the Total Electric Field across the Two Oppositely Charged Electrodes

A typical example of monomer density distribution of the two types of grafted PE chains and the total electric field profile under a positive external electric field is illustrated in Fig. 5. The peak position of the monomer density profile of the shorter PE chains is very close to the grafting electrode due to the strong electrostatic attraction from the grafting electrode. A bi-modal monomer distribution of the grafted longer PE chains emerges. Figure 5 further indicates that, compared to the bi-disperse PE brushes in the absence of external electric fields, the shorter chains are more strongly attracted to the grafting electrode than the longer chains under a strong and positive external electric field. The total electric field decays quickly away from the positively charged grafting electrode. This fast decay is due to the accumulation of negative charges on the grafted PE chains in large amount near the grafting electrode. As shown in Fig. 5, in the region around the tail of the monomer density

profile of the shorter PE chains, the total electric field is nearly zero. Thus, in this region, the external electric field is completely screened by the monomer charges. Further away from the grafting electrode, the total electric field changes sign, indicating that the charges on the grafted longer PE chains become dominant in determining the total electric field. Therefore, it is easy to understand from the definition of $F_{A(B)} = \int_0^D \phi_{A(B)}(x) \alpha_p E(x) dx$ why the strength of the total electric force acting on the shorter PE chains is larger than that on the longer PE chains.

Under a positive external electric field, a portion of counterions is expelled from the PE brush layer and enriched near the second electrode due to its electrostatic attraction (see Fig. 6). It was found from our numerical study that the total amount of counterions accumulated near the second electrode approximately equals to that of opposite surface charges on the second electrode. Thus, an overall charge compensation is maintained near the second electrode, which implies that, including the contribution of surface charges on the grafting electrode, overall charge neutrality is approximately achieved inside the PE brushes.

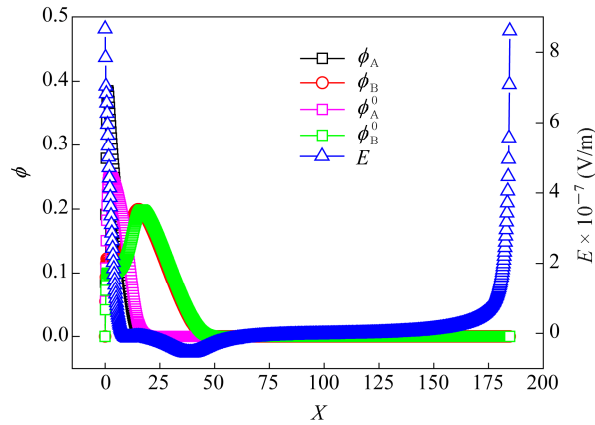


Fig. 5 Monomer density profiles of the two types PE chains and the total electric field across the two oppositely charged electrodes under a positive external electric field

In the figure, the monomer density distributions in the absence of external electric field are also displayed with ϕ_A^0 , ϕ_B^0 referring to monomer densities of chain types A and B under $E = 0$, respectively. The system parameters are $E = 9.0 \times 10^7$ V/m, $N_A = 50$, $N_B = 100$, $\alpha_p = 0.1$, $\sigma_{eA} = 0.05$ and $\sigma_{eB} = 0.05$. The x axis is in units of monomer size a .

It can be clearly seen from Fig. 7 that, the monomer density distribution of the longer PE chains (type A) is more strongly affected by a negative external electric field than that of the shorter PE chains (type B). The monomer density profile of the shorter PE chains barely changes when a negative external electric field is applied. Under a negative external electric field, the total electric field everywhere points towards the grafting electrode (negative total electric field), as shown in Fig. 7, which is in sharp contrast to the case of positive external electric field. Therefore, under such a circumstance, the strength of total electric force acting on the longer PE chains is larger than that on the shorter PE chains, which is just opposite to the case of positive external electric field. The bi-modal monomer distribution of the longer PE chains persists under a negative external electric field although it is less pronounced compared with that under a positive external electric field. As expected, all of the counterions reside inside the PE brushes due to the strong electrostatic attraction from the grafting electrode under a negative external electric field (see Fig. 8).

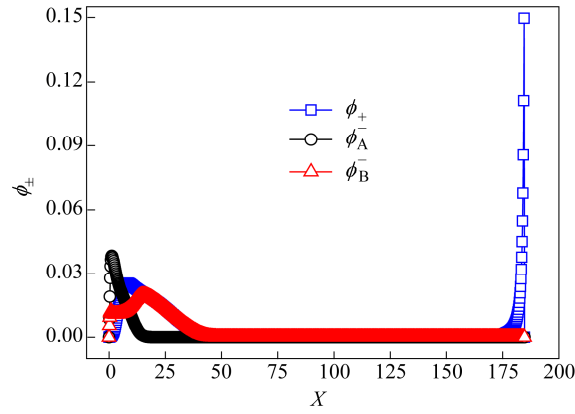


Fig. 6 Density distributions of monomer charges and counterions

Note that $\phi_A^- = \alpha_P \phi_A$, $\phi_B^- = \alpha_P \phi_B$. The system parameters are the same as those in Fig. 5.

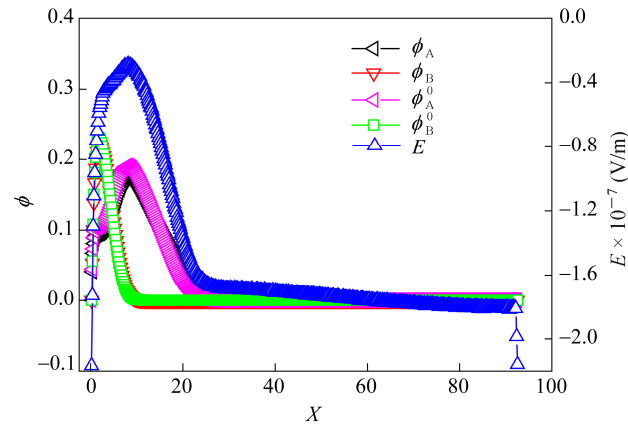


Fig. 7 Monomer density profiles of the two types PE chains and the total electric field across the two oppositely charged electrodes under a negative external electric field

In the figure, the monomer density distributions in the absence of external electric field are also displayed with ϕ_A^0 , ϕ_B^0 referring to monomer densities of chains of type A and B under $E = 0$, respectively. The system parameters are $E = -2.27 \times 10^7$ V/m, $N_A = 50$, $N_B = 20$, $\alpha_P = 0.1$, $\sigma_{gA} = 0.05$ and $\sigma_{gB} = 0.05$.

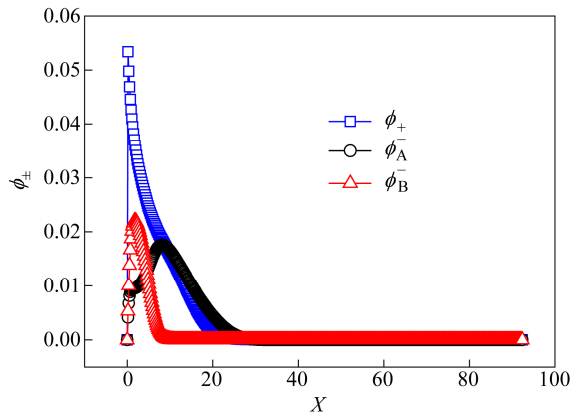


Fig. 8 Density distributions of monomer charges and counterions

Note that $\phi_A^- = \alpha_P \phi_A$, $\phi_B^- = \alpha_P \phi_B$. The system parameters are the same as those in Fig. 7.

CONCLUSIONS

The response of PE brushes to electrical stimuli is important to their applications in sensing and actuation. Polydispersity is generally an inherent characteristic of synthetic polymers. In this paper, we have performed numerical self-consistent field theory study of the response of bi-disperse PE brushes to external electric fields. The variation of brush height in response to external electric fields was examined and the total electric forces acting on grafted shorter and longer PE chains were calculated. Furthermore, monomer and counterion density distributions and the total electric field across the two oppositely charged electrodes were also computed.

Numerical results reveal that, under a positive external electric field, the response in terms of the relative change in brush height is stronger for grafted shorter PE chains than for longer PE chains in the bi-disperse brushes, and the magnitude of the total electric force acting on one shorter PE chain is larger than that on one longer PE chain. On the contrary, the opposite trends were observed for bi-disperse PE brushes under a negative external electric field. Under a positive external electric field, the total electric field decays quickly away from the positively charged grafting electrode. In the region around the tail of the monomer density profile of the shorter PE chains, the total electric field drops to nearly zero. Further away from the grafting electrode, the total electric field changes its sign, indicating that the charges on the grafted longer PE chains become the dominant factor in determining the total electric field. Therefore, under a positive external electric field, the magnitude of the total electric force acting on one shorter PE chain is larger than that on one longer PE chain, which leads to the stronger response of shorter PE chains to a positive external electric field compared with the longer PE chains. However, under a negative external electric field, the total electric field everywhere between the two oppositely charged electrodes points towards the grafting electrode (negative sign of the total electric field), which results in a stronger stretching force acting on longer PE chains compared with shorter PE chains. The stronger stretching force acting on grafted longer PE chains under a negative external electric field is consistent with the experimental result that, under a stretching external electric field, the longer ssDNA strands were detached from the Au electrode first.

REFERENCES

- 1 Napper, D.H., "Polymeric stabilization of colloidal dispersions", Academic Press, London, 1983, Vol. 7
- 2 Halperin, A., Tirrell, M. and Lodge, T.P., *Adv. Polym. Sci.*, 1991, 100: 31
- 3 Naji, A., Seidel, C. and Netz, R.R., *Adv. Polym. Sci.*, 2006, 198: 149
- 4 Borisov, O.V., Zhulina, E.B. and Birshtein, T.M., *Macromolecules*, 1994, 27: 4795
- 5 Netz, R.R. and Andelman, D., *Phys. Rep.*, 2003, 380(1-2): 1
- 6 Naji, A., Netz, R.R. and Seidel, C., *Eur. Phys. J. E*, 2003, 12: 223
- 7 Witte, K.N., Kim, S. and Won, Y.Y., *J. Phys. Chem. B*, 2009, 113: 11076
- 8 Seidel, C., *Macromolecules*, 2003, 36: 2536
- 9 Hehmeyer, O.J., Arya, G., Panagiotopoulos, A.Z. and Szleifer, I., *J. Chem. Phys.*, 2007, 126: 244902
- 10 Wynveen, A. and Likos, C.N., *Phys. Rev. E*, 2009, 80: 010801
- 11 Linse, P., *J. Chem. Phys.*, 2007, 126: 114903
- 12 Russano, D., Carrillo, J.M.Y. and Dobrynin, A.V., *Langmuir*, 2011, 27: 11044
- 13 Ou, Y.P., Sokoloff, J.B. and Stevens, M.J., *Phys. Rev. E*, 2012, 85: 011801
- 14 He, S.Z., Merlitz, H., Chen, L., Sommer, J.U. and Wu, C.X., *Macromolecules*, 2010, 43: 7845
- 15 Ibergay, C., Malfreyt, P. and Tildesley, D.J., *J. Phys. Chem. B*, 2010, 114: 7274
- 16 Wu, J.M., Zhao, S., Gao, L., Wu, J.Z. and Gao, D., *Lab Chip*, 2011, 11: 4036
- 17 Zhao, S., Wu, J.M., Gao, D. and Wu, J.Z., *J. Chem. Phys.*, 2011, 134: 065103
- 18 Wu, J.M., Zhao, S., Gao, L., Wu, J.Z. and Gao, D., *J. Phys. Chem. B*, 2013, 117: 2267
- 19 Tsori, Y., Andelman, D. and Joanny, J.F., *Europhys. Lett.*, 2008, 82: 46001

- 20 Yamamoto, T. and Pincus, P.A., *Europhys. Lett.*, 2011, 95: 48003
- 21 Migliorini, G., *Macromolecules*, 2010, 43: 9168
- 22 Cao, Q.Q., Zuo, C.C., Li, L.J. and Yan, G., *Biomicrofluidics*, 2011, 5: 044119
- 23 Ouyang, H., Xia, Z.H. and Zhe, J., *Nanotechnology*, 2009, 20: 195703
- 24 Ho, Y.F., Shendruk, T.N., Slater, G.W. and Hsiao, P.Y., *Langmuir*, 2013, 29: 2359
- 25 Merlitz, H., Li, C., Wu, C.X. and Sommer, J.U., *Soft Matter*, 2015, 11: 5688
- 26 Meng, D. and Wang, Q., *J. Chem. Phys.*, 2011, 135: 224904
- 27 Tong, C., *J. Chem. Phys.*, 2015, 143: 054903
- 28 Shi, A.C. and Noolandi, J., *Macromol. Theory Simul.*, 1999, 8(3): 214
- 29 Wang, Q., Taniguchi, T. and Fredrickson, G.H., *J. Phys. Chem. B*, 2004, 108: 6733